IONIC CONDUCTIVITY

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1. Theory

1.1. Charge transport due to self-diffusion. The *charge transport due to self-diffusion* of α-type molecule $\lambda^{\alpha}_{uncorr}$ can be calculated from Einstein relation as

$$\lambda^{\alpha}_{uncorr} V k_B T = \lim_{t\to\infty} \frac{\langle q^2_{\alpha} \left[\vec{r}_{\alpha}(t) - \vec{r}_{\alpha}(0)\right]^2 \rangle}{6t}, \tag{1}$$

where V and T are volume and temperature of the system, k_B is the Boltzmann constant, $\vec{r}_{\alpha}(t)$ is vector position at time t for one α-type molecule, and q_{α} is ionic charge of α-type molecule.

One can improve the statistical precision of results by averaging over the number of α-type molecules in the system N_{α},

$$\lambda^{\alpha}_{uncorr} = \frac{1}{V k_B T} \lim_{t\to\infty} \frac{1}{6t} \langle \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} q^2_{\alpha} \left[\vec{r}_i(t) - \vec{r}_i(0)\right]^2 \rangle. \tag{2}$$

The charge transport due to self-diffusion λ_{uncorr} is defined as

$$\lambda_{uncorr} = \frac{1}{N} \sum_{\alpha=1}^{N_{type}} N_{\alpha} \lambda^{\alpha}_{uncorr}, \tag{3}$$

where N_{type} is the number of molecules types, and N is the total number of molecules. Notice that $N = \sum_{\alpha=1}^{N_{type}} N_{\alpha}$.

1.2. **Total charge transport.** The *collective charge transport* of α-type and β-type molecules $\lambda^{\alpha\beta}$ can be calculated from Einstein relation as

$$\lambda^{\alpha\beta} V k_B T = \lim_{t\to\infty} \frac{\langle q_\alpha \left[\vec{r}_\alpha(t) - \vec{r}_\alpha(0)\right] \cdot q_\beta \left[\vec{r}_\beta(t) - \vec{r}_\beta(0)\right]\rangle}{6t}. \tag{4}$$

One can improve the statistical precision of results by averaging over the number of α-type and β-type molecules in the system N_α and N_β,

$$\lambda^{\alpha\beta} = \frac{1}{V k_B T} \lim_{t\to\infty} \frac{1}{6t} \langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} q_\alpha \left[\vec{r}_i(t) - \vec{r}_i(0)\right] \cdot \frac{1}{N_\beta} \sum_{j=1}^{N_\beta} q_\beta \left[\vec{r}_j(t) - \vec{r}_j(0)\right]\rangle. \tag{5}$$

The *total charge transport* λ is defined as

$$\lambda = \frac{1}{N} \sum_{\alpha=1}^{N_{type}} \sum_{\beta=1}^{N_{type}} N_\alpha N_\beta \lambda^{\alpha\beta}. \tag{6}$$

2. Implementation

2.1. **Charge transport due to self-diffusion.** In realizing Eq. 2 from simulation, the brackets would be interpreted as averages over *time origins*

$$\lambda^{\alpha}_{uncorr} = \frac{1}{V k_B T} \lim_{t\to\infty} \frac{1}{6t} \left\{ \lim_{\tau\to\infty} \frac{q_\alpha^2}{N_\alpha \tau} \sum_{i=1}^{N_\alpha} \int_0^\tau \left[\vec{r}_i(t_0 + t) - \vec{r}_i(t_0)\right]^2 dt_0 \right\}. \tag{7}$$

In simulations, one uses discrete time steps, so that one has a set of discrete times $\{t_1, t_2, \ldots, t_{N_{tot}}\}$, where $t_i = t_0 + (i-1)\Delta t$ for $i = 1, 2, \ldots, N_{tot}$ and Δt is the *time step*. *Total time simulation* is given by $t_{simul} = t_{N_{tot}} - t_1$. Time origins belong to set of discrete times $\{t_1, t_2, \ldots, t_{N_{or}}\}$, where $N_{or} = \frac{N_{tot}}{2}$. *Elapsed time* is set equal to $t = n\Delta t$, where $n = 1, 2, \ldots, N_{or}$. Thus,

$$\lambda^{\alpha}_{uncorr} = \lim_{t\to\infty} \lambda^{\alpha}_{uncorr}(t), \tag{8}$$

where

$$\lambda^{\alpha}_{uncorr}(t) = \frac{e^2}{6tVk_BT} \frac{z_\alpha^2}{N_\alpha N_{or}} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_{or}} \left[\vec{r}_i(t_j + t) - \vec{r}_i(t_j)\right]^2. \tag{9}$$

Note that $q_\alpha = z_\alpha e$ where e is the elementary charge.

Using Eqs. 8 and 9 into Eq. 3, one can define

$$\lambda_{uncorr} = \lim_{t\to\infty} \lambda_{uncorr}(t) \tag{10}$$

where

$$\lambda_{uncorr}(t) = \frac{e^2}{6tVk_BTNN_{or}} \sum_{\alpha=1}^{N_{type}} z_\alpha^2 \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_{or}} \left[\vec{r}_i(t_j + t) - \vec{r}_i(t_j)\right]^2. \tag{11}$$

From *apparent* self-diffusion constant of α-type molecule $D_\alpha(t)$, Eq. 11 can be written as

$$\lambda_{uncorr}(t) = \frac{e^2}{V k_B T} \sum_{\alpha=1}^{N_{type}} z_\alpha^2 n_\alpha D_\alpha(t), \tag{12}$$

where $n_\alpha = N_\alpha / N$.

2.2. **Total charge transport.** In realizing Eq. 5 from simulation, the brackets would be interpreted as averages over *time origins*

(13)

$$\lambda^{\alpha\beta} = \frac{1}{V k_B T} \lim_{t\to\infty} \frac{1}{6t} \left\{ \lim_{\tau\to\infty} \frac{q_\alpha q_\beta}{N_\alpha N_\beta \tau} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \int_0^\tau \left[\vec{r}_i(t_0+t) - \vec{r}_i(t_0)\right] \cdot \left[\vec{r}_j(t_0+t) - \vec{r}_j(t_0)\right] dt_0 \right\}.$$

In simulations, one uses discrete time steps, so that one has a set of discrete times $\{t_1, t_2, \ldots, t_{N_{tot}}\}$, where $t_i = t_0 + (i-1)\Delta t$ for $i = 1, 2, \ldots, N_{tot}$ and Δt is the *time step.* *Total time simulation* is given by $t_{simul} = t_{N_{tot}} - t_1$. Time origins belong to set of discrete times $\{t_1, t_2, \ldots, t_{N_{or}}\}$, where $N_{or} = \frac{N_{tot}}{2}$. *Elapsed time* is set equal to $t = n\Delta t$, where $n = 1, 2, \ldots, N_{or}$. Thus,

$$\lambda^{\alpha\beta} = \lim_{t\to\infty} \lambda^{\alpha\beta}(t), \tag{14}$$

where

(15)

$$\lambda^{\alpha\beta}(t) = \frac{e^2}{6tVk_BT} \frac{z_\alpha z_\beta}{N_\alpha N_\beta N_{or}} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \sum_{k=1}^{N_{or}} \left[\vec{r}_i(t_k+t) - \vec{r}_i(t_k)\right] \cdot \left[\vec{r}_j(t_k+t) - \vec{r}_j(t_k)\right].$$

Using Eqs. 14 and 15 into Eq. 6, one can define

$$\lambda = \lim_{t\to\infty} \lambda(t) \tag{16}$$

where

(17)

$$\lambda(t) = \frac{e^2}{6tVk_BTNN_{or}} \sum_{\alpha=1}^{N_{type}} z_\alpha \sum_{\beta=1}^{N_{type}} z_\beta \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\alpha} \sum_{k=1}^{N_{or}} \left[\vec{r}_i(t_k+t) - \vec{r}_i(t_k)\right] \cdot \left[\vec{r}_j(t_k+t) - \vec{r}_j(t_k)\right].$$

For practical reasons, one defines the *degree of uncorrelated ion motion* as

$$\gamma_d = \lim_{t\to\infty} \gamma_d(t), \tag{18}$$

where

$$\gamma_d(t) = \frac{\lambda(t)}{\lambda_{uncorr}(t)}. \tag{19}$$

Then, one calculates $\lambda_{uncorr}(t)$ from Eq. 12 using diffusion coefficients corrected for the finite simulation cell size as well as *apparent* degree of uncorrelated ion motion $\gamma_d(t)$. Finally, *apparent* total charge transport $\lambda(t)$ is obtained from Eq. 19.